

A Molecular Dynamics Investigation of the Structural Characteristics of Amorphous and Annealed Poly(Vinylidene Fluoride) and Vinylidene Fluoride-Trifluoroethylene Copolymers

Robert W. Holman
George J. Kavarnos
Submarine Sonar Department



19950511 076

Naval Undersea Warfare Center Division
Newport, Rhode Island

Approved for public release; distribution is unlimited.

PREFACE

The work described in this report was sponsored by the Naval Undersea Warfare Center's (NUWC's) Independent Research (IR) Program, as Project No. A10016 entitled "Molecular Modeling of New Transducer Materials." The IR Program is funded by the Office of Naval Research; the NUWC program manager is Dr. Kenneth M. Lima (Code 102).

The technical reviewer for this report was Thomas Ramotowski (Code 2131).

The authors acknowledge the support of the United States Navy-American Society for Engineering Education (ASEE) Summer Faculty Research Program. (Co-author R. W. Holman, who participated in the Navy ASEE Summer Faculty program, may be contacted at Western Kentucky University, Department of Chemistry, Bowling Green, Kentucky 42101.)

Reviewed and Approved: 17 April 1995



R. J. Martin
Head, Submarine Sonar Department (*acting*)

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)			2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
			17 April 1995	Final
4. TITLE AND SUBTITLE A Molecular Dynamics Investigation of the Structural Characteristics of Amorphous and Annealed Poly(Vinylidene Fluoride) and Vinylidene Fluoride-Trifluoroethylene Copolymers			5. FUNDING NUMBERS PR A10016	
6. AUTHOR(S) R. W. Holman (ASEE Summer Faculty) and G. J. Kavarnos				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Undersea Warfare Center Detachment 39 Smith Street New London, Connecticut 06320-5594			8. PERFORMING ORGANIZATION REPORT NUMBER TR 10,857	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Undersea Warfare Center Division 1176 Howell Street Newport, Rhode Island 02841-5594			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Molecular dynamics (MD) computations predict that the percentage of <i>gauche</i> bonds for poly(vinylidene fluoride) [PVDF] is greater than that for the 50 mol% copolymer with trifluoroethylene, at high temperature and after annealing. PVDF is enriched in <i>gauche</i> conformations on cooling whereas the copolymer acquires more <i>trans</i> conformations. The MD results are consistent with experimental trends that have been observed for these piezoelectric polymers.				
14. SUBJECT TERMS Molecular Dynamics Piezoelectric Polymers			15. NUMBER OF PAGES 22	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR	

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS	ii
LIST OF TABLES	iii
INTRODUCTION	1
THEORY AND BACKGROUND	2
Nature of the Polymers Investigated	2
General Background Regarding Polymer Structure/Property Relationships	2
General Background of Polymer Structural Analysis	2
Detailed Structural Characteristics of Polymers Investigated	3
EXPERIMENTAL	5
The Molecular Dynamics Approach	5
Computational Methodology	7
Simulation Conditions	7
RESULTS AND DISCUSSION	8
Molecular Dynamics of Related Dimers	8
Molecular Dynamics of Single-Chain Polymers	9
Molecular Dynamics of Modified Single-Chain Polymers	10
Elongation of <i>tgtg'</i> PVDF	11
CONCLUSIONS	11
REFERENCES	21

Accesion For	
NTIS	CRA&I <input checked="" type="checkbox"/>
DTIC	TAB <input type="checkbox"/>
Unannounced <input type="checkbox"/>	
Justification _____	
By _____	
Distribution / _____	
Availability Codes	
Dist	Avail and / or Special
<i>A-1</i>	

LIST OF ILLUSTRATIONS

Figure	Page
1 Structures of PVDF α - and β -Phase Polymorphs	13
2 Histogram Showing Distribution of Dihedrals of Hot and Cold PVDF	14
3 Histogram Showing Distribution of Dihedrals of Hot and Cold 50 mol% P(VDF-TrFE) Copolymer	15
4 Histogram Showing Distribution of Dihedrals of Hot PVDF vs. Hot 50 mol% P(VDF-TrFE)	16
5 Histogram Showing Distribution of Dihedrals After Annealing	17
6 Energy Diagram	18

LIST OF TABLES

Table		Page
1	Calculated Dihedral Angles of Simple Dimers	19
2	Calculated <i>gauche</i> - and <i>trans</i> -Dihedral Angles of 1,28-Methylene Unit Single Chain Polymers	19
3	Calculated <i>gauche</i> - and <i>trans</i> -Dihedral Angles of U-Shaped Polymers	20
4	Elongation of a <i>tgtg'</i> PVDF Tetramer as Monitored by Geometry Optimization	20

A MOLECULAR DYNAMICS INVESTIGATION OF THE STRUCTURAL CHARACTERISTICS OF AMORPHOUS AND ANNEALED POLY(VINYLIDENE FLUORIDE) AND VINYLIDENE FLUORIDE- TRIFLUOROETHYLENE COPOLYMERS

INTRODUCTION

The Navy has long been interested in the polymers poly(vinylidene fluoride), PVDF, and poly(vinylidene fluoride/trifluoroethylene), P(VDF-TrFE), because of their piezoelectric properties, which make them potential candidate materials for active and passive underwater transducers. Research results from Naval Undersea Warfare Center Division, Detachment, and other laboratories have demonstrated that these materials hold great promise with their prime advantage over existing piezoelectric materials being their low mass, high processability, and low cost. However, experimentally it is difficult to identify and optimize the crystallization and annealing conditions utilized in the construction of these polymers.

Within this laboratory both applied and theoretical investigations are ongoing with the focus towards an increased understanding of these materials. The goal of the project reported here was to gain insight into the molecular structure of the two related polymers. Specific interest lays in establishing structure/property relationships to ultimately make predictable the ideal crystallization/annealing conditions for specific applications as a function of polymer composition.

Details of polymer processes at the atomic or molecular level are important for a more thorough understanding of bulk material properties. However, these details are not directly accessible experimentally because the specific motions of atoms in a polymer cannot readily be evaluated by traditional laboratory techniques. As an alternative, one can consider computational molecular modeling. The theoretical method of choice in the investigation reported upon here was the molecular dynamics (MD) methodology. Computer simulations employing MD allow for the elucidation of dynamic structural change of polymers at the molecular level as a function of temperature. In this communication, we report on the MD analysis of the structures of PVDF and P(VDF-TrFE) as a function of temperature and relate the results to the crystallization processes observed experimentally for each of the polymers.

THEORY AND BACKGROUND

NATURE OF THE POLYMERS INVESTIGATED

The polymer PVDF consists of many repeating units of the monomer vinylidene fluoride, VDF. When VDF monomer units are mixed and reacted with a second monomer unit, trifluoroethylene, TrFE, the copolymer P(VDF-TrFE) is formed. Numerous copolymers can be constructed differing from one another in the relative proportions of the two monomers as well as their connectivity. The composition of the copolymer is reported as the percent moles (%mol) of vinylidene fluoride. For example, 75 mol% P(VDF-TrFE) designates a composition with a VDF/TrFE mole ratio of 3:1. The most suitable compositions for underwater piezoelectric applications are those with VDF levels between 60 and 90 mol%, as has been shown by an earlier molecular modeling investigation in this laboratory.^{1,2} For many sonar applications, P(VDF-TrFE) copolymers are superior to PVDF because the latter requires mechanical stretching prior to poling, adding substantially to fabrication costs. Because the copolymers can be poled without stretching, they can be solvent-cast or injection-molded into desired geometries and thicknesses in a simple and low-cost manner.³

GENERAL BACKGROUND REGARDING POLYMER STRUCTURE/PROPERTY RELATIONSHIPS

Long-chain molecules (polymers) can exist in two general states. In the liquid state there is normally no long range order, and chain bonds adopt rotational angles that are dictated by energetics and statistical mechanics, leading to the evolution of random structures.⁴ The centers of gravity of the chains themselves are also randomly distributed relative to one another. However, under appropriate conditions, a chain with sufficient periodicity can develop order along a portion of its length. An ensemble of such chain segments can then order itself into a three dimensional array, and the system is said to have crystallized.⁵ The characteristic macroscopic consequence of a bulk polymer possessing considerable liquid-like or amorphous character is rubber-like elasticity. In contrast, bulk polymers of high crystallinity tend not towards elasticity but rigidity. Many organic polymers are semi-crystalline, possessing both amorphous and crystalline character, and macroscopic properties are intimately related to the degree of crystallinity.

GENERAL BACKGROUND OF POLYMER STRUCTURAL ANALYSIS

The spatial arrangement of atoms in a molecule, designated by the term configuration, is specified in terms of the coordinates within three-dimensional space for each atom. The coordinates of the atoms within the molecule are governed by the

nature of the atom-to-atom connectivity, or chemical bonding between atoms. Specifically, the lengths of bonds and the angles between bonds meeting at a given atom (bond angles) are restricted within a narrow range. The potentials affecting rotations about chemical bonds are less restrictive than those governing either bond lengths or angles. Large molecules, such as polymers, owing to rotation about bonds of the molecular framework, possess an array of configurations, or conformations. The term conformation, for purposes here, relates most specifically to the torsional (dihedral) angles of the polymer chain. The polymer can be described as a continual array of dihedral angles going from one end of a chain to its terminus. (A dihedral angle is the bond rotation angle around the axis of the center two carbon atoms between two planes, each defined by the center bond and one terminal, as in C-C-C-C.) One conformation for a given polymer may have repeating C-C-C-C dihedral angles of some value X, while a second conformation for the same polymer may have a repeating motif with a dihedral of Y. These specific conformations of the same polymer, called polymorphs, are not necessarily of equal energy, and can interconvert as a function of many variables (temperature, elongation, presence or absence of solvent or plasticizers, etc.). Specific polymorphs for a given chemical composition are typically designated with Greek prefixes (i.e., the PVDF α -phase, or PVDF β -phase) and are typically further specified with terminology relating to the repeating dihedrals. The specific dihedral nomenclature pertinent here is designated as follows: t = *trans* or $\sim 180^\circ$ dihedral, and g = *gauche* or $\sim 45 - 90^\circ$ dihedrals.

The key point of the above treatment is this: from the viewpoint of fundamental polymer chemistry, the macroscopic properties of the material are often determined as much by the polymer molecular conformation (i.e., polymorph) as its chemical composition.

DETAILED STRUCTURAL CHARACTERISTICS OF POLYMERS INVESTIGATED

When PVDF is either crystallized from the melt or solvent cast, the predominant polymorph that initially forms is called the α -phase.⁶ The conformation of the polymer segments within the crystalline α -phase unit cell is $tgtg'$, with the chains oriented in the cell such that no net polarization exists for the cell (figure 1). On the basis of an early X-ray crystallography investigation, Hasegawa and coworkers proposed that the PVDF α -phase is a distorted $tgtg'$ structure, with a carbon dihedral repeating motif of 179° and 45° .⁷ Doll, Lando, and Bachmann proposed a more "ideal" $tgtg'$ conformation with g and g' angles of $\sim 60^\circ$.^{8,9} When PVDF is uniaxially elongated, the α -phase undergoes polymorphism to the β -phase. Hasegawa proposed that the β -phase conformation is a slightly distorted all-*trans*, planar zig-zag with an alternating 172° and -172° repeating motif.⁷ In the β -phase, the polymer segments are oriented such that the C-F dipoles are additive, resulting in a polar unit cell (figure 1). Hence, to become piezoelectric, PVDF must be uniaxially elongated (to induce α -

to β -phase polymorphism) after initial crystallization and prior to electroprocessing. In contrast, the copolymers crystallize directly into a β -phase that possesses a polar unit cell. The copolymers can be electroprocessed into a piezoelectric material immediately after crystallization.

Several theoretical investigations have confirmed the existence of polymorphism in PVDF. Karasawa and Goddard,¹⁰ using Hartree-Fock calculations and experimental phonon frequencies, recently reported that the differences in energies between four polymorphs of PVDF (including the α - and β -phases) are within 1 kcal/mol/monomer. Farmer, Hopfinger, and Lando,¹¹ using potential energy calculations to determine the chain conformation and packing energies, confirmed that conversions between the α - and β -phases should be energetically feasible, but that increasing the concentration of head-to-head defects in PVDF should favor formation of the β -phase.

The central focus of our ongoing work deals with the structural implications of increasing fluorine content in P(VDF-TrFE) copolymers. The fluorine content of the copolymer can be readily controlled by altering the mol percent of TrFE with respect to VDF in the generation of the copolymer. We recently reported results from molecular mechanics calculations using the MM2 force field of Allinger¹² and crystal packing simulations relating to: (1) the effect of fluorine content on the intramolecular energy of PVDF and various copolymer chain segments; and (2) the relative energies of PVDF and copolymer crystallites.²

The intramolecular energies for polymer chain segments were found to increase with increasing fluorine content independent of conformation (Hasegawa or "ideal"). Interestingly, for PVDF, the Hasegawa *tgtg'* conformation is more stable than the Hasegawa and "ideal" all-*trans* structures. In contrast, the "ideal" all-*trans* conformations are favored for each of the copolymers. The crossover point corresponding to the composition where the Hasagawa all-*trans* conformation becomes favored over the *tgtg'* conformation is ~90 mol% VDF. In comparing the crystal packing energies for the Hasegawa and "ideal" *tgtg'* crystal structures, the Hasegawa polymorphs are favored for all compositions. The extent to which the Hasegawa *tgtg'* is preferred decreases somewhat with increasing fluorine content.

The salient finding from our previous work that serves as the motivation for the present investigation is the fact that the PVDF all-*trans* conformation (which, as an isolated small polymer, is less stable than the *tgtg'*) packs more favorably into a unit cell than the Hasegawa *tgtg'* conformation. Thus, it may be that the all-*trans* polymorph is the global energy minimum for PVDF even though the polymer is known to crystallize from the melt into a *tgtg'* repeating motif. Thus, it is reasonable to assess whether intramolecular interactions exert kinetic control on the crystal-

lization behavior of the polymer. We report here the results from a molecular dynamics perspective on the amorphous and the annealed structures for PVDF and 50 mol% P(VDF-TrFE).

EXPERIMENTAL

THE MOLECULAR DYNAMICS APPROACH

In a molecular dynamics or MD simulation, a computer algorithm is used to calculate the future positions and momenta of every atom in a molecule based on current positions and momenta.¹³ The positions and momenta are continually propagated in a series of equally-spaced time intervals for a finite time chosen by the experimentalist. In this fashion, it is possible to simulate conformational change within a polymer as a function of temperature (i.e. mimicking crystallization and/or annealing) in a dynamic fashion while monitoring potential energy, kinetic energies, dihedrals, chain length change with time, etc.

In the MD approach, Hamilton's equations of motion are solved. The simulation first determines the force on each atom (f_i) from all of the other atoms as a function of time at a certain temperature:

$$F_i = -\frac{\partial V}{\partial r_i}, \quad (1)$$

where V is a potential energy function and r_i is the position of atom i . Then the acceleration, a_i , of each atom is determined by dividing the force acting on it by the mass of the atom, m_i ,

$$a_i = \frac{f_i}{m_i}. \quad (2)$$

The approach employed in the present work is called the leap-frog algorithm. This algorithm updates the positions of atoms and the velocities for the next step by

the following equation:

$$v_i(t + \frac{1}{2}\Delta t) = v_i(t - \frac{1}{2}\Delta t) + \Delta t a_i(t). \quad (3)$$

Let $v_{-1/2}$ be the first guess of a velocity at $t_o - 1/2\Delta t$ and x_o be the position at time t_o . The "new" velocity $v_{1/2}$ is therefore

$$v_{1/2} = v_{-1/2} + a_o \Delta t, \quad (4)$$

and the "new" coordinate x_1 is

$$x_1 = x_o + v_{1/2} \Delta t. \quad (5)$$

New velocities and positions can be specified continuously as shown below:

$$v_{3/2} = v_{1/2} + a_1 \Delta t, \quad (6)$$

and

$$x_2 = x_1 + v_{3/2} \Delta t. \quad (7)$$

At each integral time, the new coordinates (represented by x above) and the accelerations are calculated; at half integral times, the velocities are determined. The molecular dynamics trajectory can be visualized as a set of atoms with specific coordinates and velocities evolving according to equations (3) to (7).

The kinetic energy (K) is then defined in terms of the velocities and masses of

the atoms, i.e.,

$$K = \frac{1}{2} m_i v_i^2. \quad (8)$$

The kinetic energy at time t is calculated using the current velocity, which is approximated by

$$v_i(t) = \frac{1}{2} [v_i(t + \frac{1}{2} \Delta t) + v_i(t - \frac{1}{2} \Delta t)]. \quad (9)$$

The total energy of the system, or Hamiltonian, is the sum of the kinetic and potential energies:

$$H(r, p) = K(p) + V(p), \quad (10)$$

where r is a set of Cartesian coordinates and p is the momenta of the atoms.

In a typical molecular dynamics simulation, the positions and velocities are assigned to the atoms. The velocities reflect the target temperature for the simulation. Equilibration proceeds with partition between potential and kinetic energy and a thermal distribution of velocities. Equilibration may involve thousands of time steps. In the production part of the run, as time evolves, the coordinates and velocities at each time step are stored. This part of the analysis allows the study of the properties and geometries of new structures as they emerge with time.

COMPUTATIONAL METHODOLOGY

All computations were performed on a Silicon Graphics 4D/35 IRIS workstation utilizing commercial software produced by Hypercube (HYPERCHEMA) and Cerius. The MD computations were performed at the MM+ level utilizing the force field of Burkert and Allinger.¹⁴ All structures were evaluated atomistically.

SIMULATION CONDITIONS

Two criteria were utilized in determining the optimum temperature for the simulations of the amorphous polymers. First, the dihedral angles of the structure, upon heating, must not exhibit "memory effects" with respect to the input structure

(i.e., all of the dihedral angles within the structure must change markedly from the input dihedrals as evidenced by real-time observation of the dynamic structure as it is heated). Second, heating the structure slightly above or slightly below the chosen temperature should not change the distribution of dihedral angles significantly from those attained at the chosen temperature. Both of these criteria were chosen in order to simulate, as closely as possible, the melt conditions of the polymer. The heating temperatures utilized do not quantitatively relate to their real-world analogs (i.e., an input temperature of 1800 K does not relate at all to a real-world temperature of 1800 K), but rather represent values utilized by the program to manipulate the extent of atom displacement per cycle. At a heating temperature of 2200 K, the chain structure begins to distort (i.e., begins to change bond lengths and/or angles in an unrealistic fashion), while at temperatures below 1650 K memory effects seem to be present. At temperatures between 1700 and 2100 K, the trends in the distribution of dihedral angles are similar, although not identical. The relative trends in structure as a function of temperature (from hot to cold), whether from 2000 K to 270 K, or from 1750 K to 270 K, do not qualitatively change. In view of these considerations, the temperature chosen for all simulations was 2000 K. The 1 picosecond (ps) heating time was chosen for expediency as longer heating times produced similar results, since longer times use considerable computer time. Once the polymer was heated, it was allowed to equilibrate for 3 ps. The 3 ps equilibration period was chosen because, based on these observations, it was well into the region in which the kinetic, potential, and total energies of the system were constant (1 ps would have been sufficient based upon this criterion). It should be noted that the choice of a trajectory length of the order of picoseconds imposes a limitation on a molecular dynamics simulation, in that only molecular motions occurring on a short time-scale 4, such as bond stretching vibrations, are sampled. Only changes in atomic positions are monitored in the picosecond regime.

In simulating the annealing of the polymers, a 10 ps cooling time was utilized in going from 2000 K to 270 K. This represents a rather slow annealing and is typical of simulations of this nature.

RESULTS AND DISCUSSION

MOLECULAR DYNAMICS OF RELATED DIMERS

As a preamble to evaluating polymers, a simplified MD investigation of the dimers of vinylidene fluoride and vinylidene fluoride/trifluoroethylene was undertaken. Each dimer initially possessed a 180 degree C-C-C-C dihedral angle. The input structures were heated to high temperature (2000 K) over a 1 ps time frame and allowed to equilibrate at that temperature for an additional 3 ps, at which point the dihedral angle was evaluated. Then the structure was allowed to anneal for a 10 ps time frame to 300 K, and again the dihedral angle was evaluated. From table 1, it

is clear that the hot vinylidene fluoride dimer possesses a *gauche* conformation which upon annealing remains *gauche*, whereas the hot vinylidene fluoride/trifluoroethylene dimer possesses a *gauche* conformation which upon cooling becomes *trans*.

MOLECULAR DYNAMICS OF SINGLE-CHAIN POLYMERS

In an effort to model a small PVDF polymer whose structure is reflective of the amorphous polymer (i.e., from the melt), a 128 methylene-unit long end-capped polymer was generated (initially with an all-*trans* structure) and heated to high temperature (2000 K) over a 1 ps time frame and allowed to equilibrate at that temperature for an additional 3 ps. In the evaluation of the resulting structure, the C-C-C-C dihedral angles were analyzed (as absolute values such that both -45° and 45° are reported as 45°, 170° and -170° reported as 170°, etc.). The results (table 2) reveal a preference for *trans*-like dihedrals (between 145° and 180°), although the structure is also rich in *gauche*-like bonds (dihedrals between 37° and 90°). The *gauche/trans*, or *g/t* ratio for the amorphous polymer is 0.73, suggesting that the polymer at high temperature has substantial *gauche*-character.

When the above polymer is allowed to anneal over a long time frame (10 ps), it adopts a new conformational structure. The analysis of the dihedrals indicates that the polymer becomes more ordered upon cooling in that the percent of dihedrals other than those that are either *trans*- or *gauche*-like is reduced (from 24% to 2%). The percent of contribution from both *trans*- and *gauche*-like bonds increases with cooling, though the magnitude of the increase for *gauche*-like bonds is greater (table 2). Thus, the *g/t* ratio of the annealed structure is increased upon cooling (*g/t* = 0.82 for the annealed and 0.73 for the hot polymer). In figure 2, a histogram comparing the dihedrals associated with both the hot and cold PVDF and the trends leading to greater order and enrichment in *gauche*-character with cooling are graphically represented.

An identical approach was used in the analysis of 50 mol% P(VDF-TrFE), the results of which are shown in figure 3 and table 2. Once again, the polymer becomes much more ordered upon cooling. However, unlike PVDF, the percent *trans* character increases dramatically upon cooling but the percent *gauche* character remains constant (table 2). Thus, the resulting *g/t* ratios indicate that the copolymer is enriched in *trans*-character upon cooling (*g/t* for amorphous structure is 0.64 while that for the annealed structure is 0.46).

In comparing hot PVDF to hot P(VDF-TrFE), the PVDF is only slightly richer in *gauche* conformations (figure 4). In figure 5, the comparison between the two polymers after annealing reveals the same trend (that PVDF is richer in *gauche*-character). On cooling, the homopolymer becomes richer in *gauche*-character, whereas cooling the copolymer does not produce any additional *gauche* bonds. These results,

which are in accord with the experimental trends observed upon the cooling of both PVDF and 50 mol% P(VDF-TrFE),⁶ are probably due to the differences in bond, angle, torsional, van der Waal, and electrostatic energies between PVDF and the more fluorinated copolymers.

MOLECULAR DYNAMICS OF MODIFIED SINGLE-CHAIN POLYMERS

A modified starting structure for PVDF, one with a *tgtg'* repeating motif, was utilized to compare with the results from the earlier all-*trans* PVDF. This structure was chosen for investigation because the *tgtg'* polymorph for PVDF is well known.⁷ When the *tgtg'* PVDF structure is first heated and then annealed under the identical conditions as those stated earlier, the *g/t* ratio increases from 0.69 to 0.90 (amorphous and annealed, respectively, in agreement with results from the earlier experiment utilizing the all-*trans* PVDF input structure).

A second type of modified input structure was also utilized, based upon an insight gained on having evaluated the aforementioned single-chain polymers. In each of the single-chain structures investigated, the polymers bend back upon themselves a number of times such that small regions of the chain are interacting with one another. The extent of chain folding is small and difficult to quantitate for 128 methylene-unit polymers. However, were it feasible to evaluate much longer polymers, it is likely that the effect would be more pronounced. Because investigating larger polymers is impractical (because computational times measured in weeks would be required), an alternative input structure was utilized. The structure possesses two parallel and dynamic chain segments (~7 Å apart) where one end of each chain segment is tethered to a common, fixed U-shaped link. This structure makes possible a simulation that includes enhanced intermolecular interaction because the two chain segments are parallel, in close proximity to one another, and dynamic.

The analysis of the U-shaped PVDF polymer reveals that the structure becomes more ordered upon cooling with an increase in both the percent contribution from *trans*- and *gauche*-like bonds (table 3). The *g/t* ratio for amorphous "folded over" U-shaped PVDF is 0.64, which, upon annealing, remains relatively constant (changing only slightly to 0.65). The analysis of the U-shaped 50 mol% copolymer again reveals increased order upon cooling, with the *g/t* ratio remaining constant at 0.53 (the structures themselves change, though the statistical ratio remains the same). That PVDF possesses greater *gauche*-character in both the amorphous and annealed structures than does the copolymer is consistent with both the single chain computations and the experimental behavior of the true polymers.⁶

ELONGATION OF *tgtg'* PVDF

When PVDF is cast as a thin film, it initially possesses a *tgtg'* repeating motif, consistent with both the results of our earlier investigation² regarding crystal packing and the MD results of this study. When the thin film is mechanically stretched, the initial *tgtg'* structure undergoes polymorphism to an all-*trans* structure.⁶ To model such a phenomenon, a *tgtg'* PVDF tetramer was constructed with initial dihedral angles at 45°, 180°, -45°, 180° (corresponding to the Hasagawa distorted *tgtg'* geometry experimentally observed for PVDF crystallites⁷ based upon x-ray defraction and consistent with our earlier crystal packing computations²). All bond angles and distances were then allowed to relax *via* geometry optimization (with fixed dihedrals). The procedure for geometry optimization is discussed in an earlier report.¹ The resulting structure possessed an end-to-end distance of 9.252 Å. This initial structure was then incrementally elongated in 0.25 Å steps to an ultimate end-to-end distance of 10.252 Å. With each elongation, the complete structure was allowed to relax (with the end-to-end distance fixed), mimicking the elongation of the crystallite. Throughout the elongation, all the C-C-C-C dihedral angles were monitored. From table 4, a clear and systematic polymorphism from the *tgtg'* structure to an all-*trans*-like structure is evident as each *gauche* bond smoothly converts to a *trans* bond upon elongation.

CONCLUSIONS

In an earlier study, we used molecular modeling calculations to show that energetics plays a major role in determining the conformational nature of the predominant polymorph as PVDF or its copolymer with trifluoroethylene is annealed from the melt or solution.^{1,2} Although calculations of intramolecular steric energies were consistent with the crystallization behavior of PVDF and its copolymer, crystal packing energies suggested that the all-*trans* polymorph is the global minimum structure for PVDF and P(VDF-TrFE). The lack of agreement between the experimental observation that PVDF is favored to crystallize directly into the α -phase rather than the β -phase suggested to us the possibility of a kinetic barrier hindering the formation of the more thermodynamically-stable β -phase. The MD simulations reported here confirm that crystallization and crystal packing of PVDF and the copolymers is kinetically controlled. Theoretically, these calculations suggest that the PVDF α -phase is indeed a metastable state, and that the barriers for formation of the all-*trans* are much higher for PVDF than for the copolymers (figure 6). The kinetic barriers for formation of this state probably consist of unfavorable torsional conformations. On the practical side, this result explains why mechanical stretching along the polymer backbone is a requirement for formation of the piezoelectric β -phase of PVDF and not for the copolymers. As summarized in figure 6, the pathway to the PVDF β -phase must proceed directly through the α -phase, whereas for the copolymers direct crystallization into the β -phase is the favored route. The nature of the conformational

barriers separating the α - and β -phases in PVDF has yet to be elucidated. However, as suggested by Flory in his classic work,⁴ very small differences in the energies of *gauche* and *trans* conformations in fluoroalkanes may lead to rather dramatic differences in their physical properties. No doubt these small differences play a vital role in the annealing and crystallization behavior of PVDF and P(VDF-TrFE).

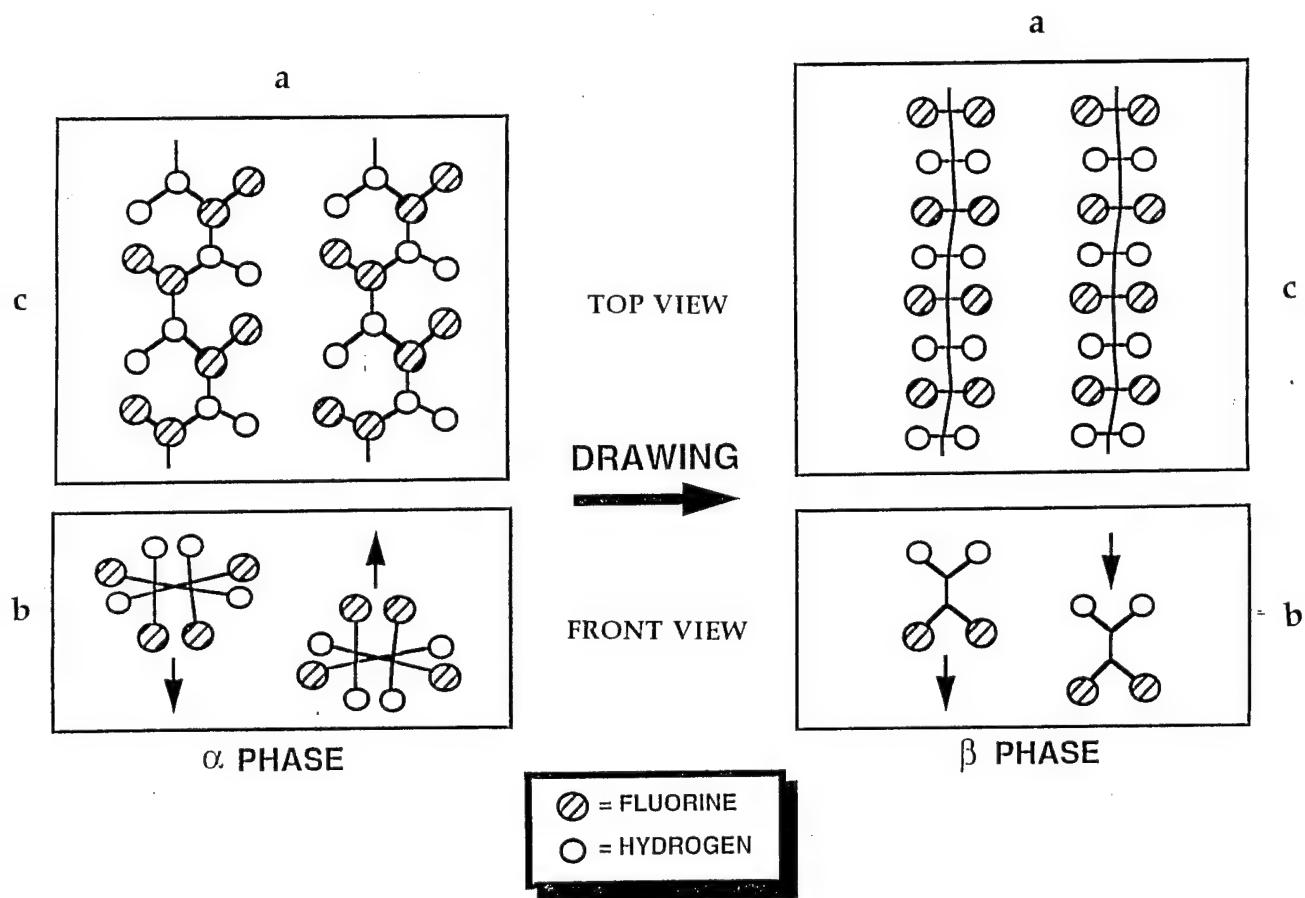


Figure 1. Structures of PVDF α - and β -Phase Polymorphs

Hot PVDF vs. Cool PVDF

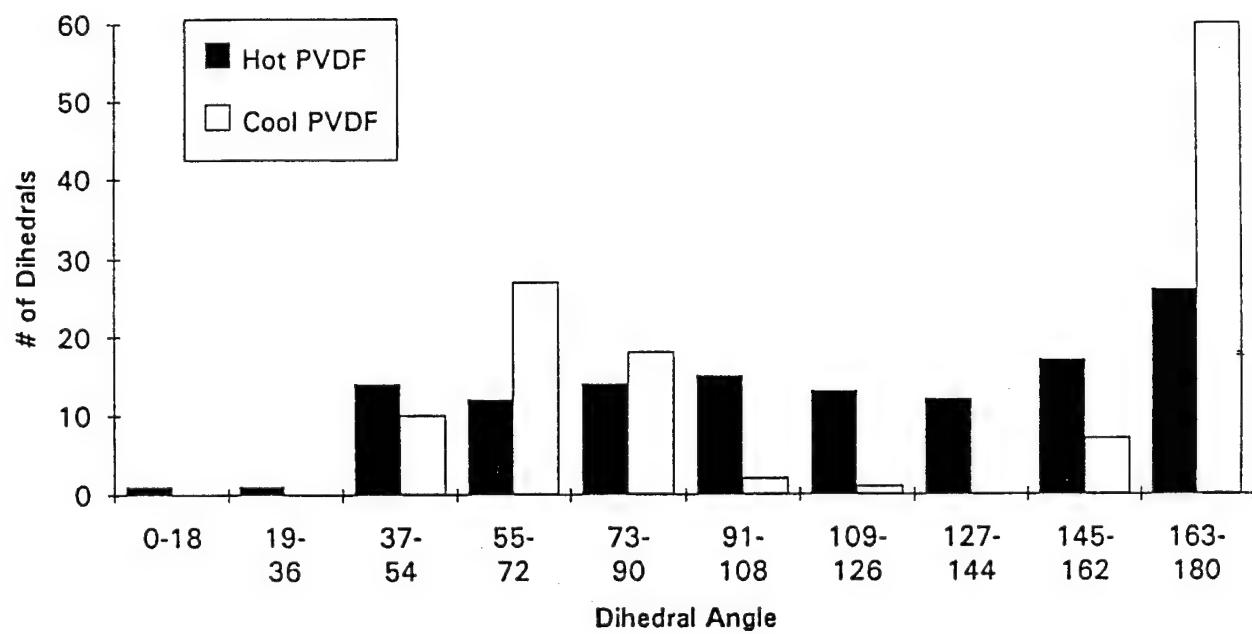


Figure 2. Histogram Showing Distribution of Dihedrals of Hot and Cold PVDF

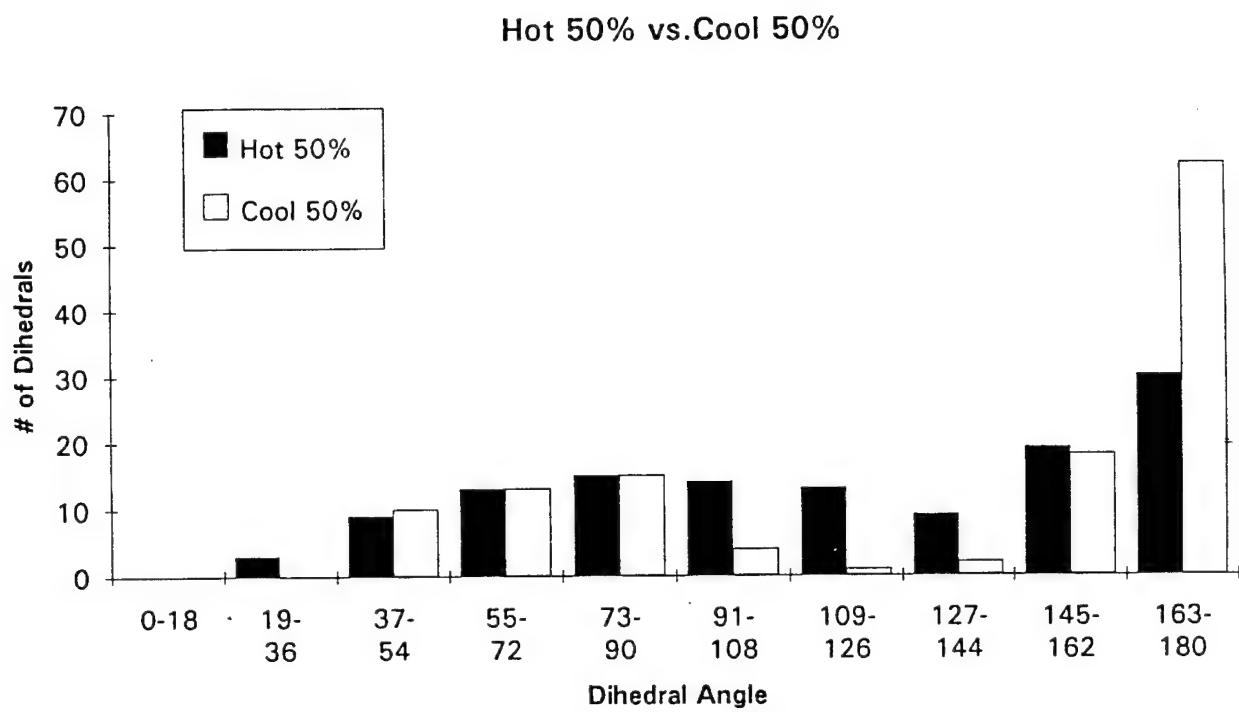


Figure 3. Histogram Showing Distribution of Dihedrals of Hot and Cold 50 mol% P(VDF-TrFE) Copolymer

Hot PVDF vs. Hot 50%

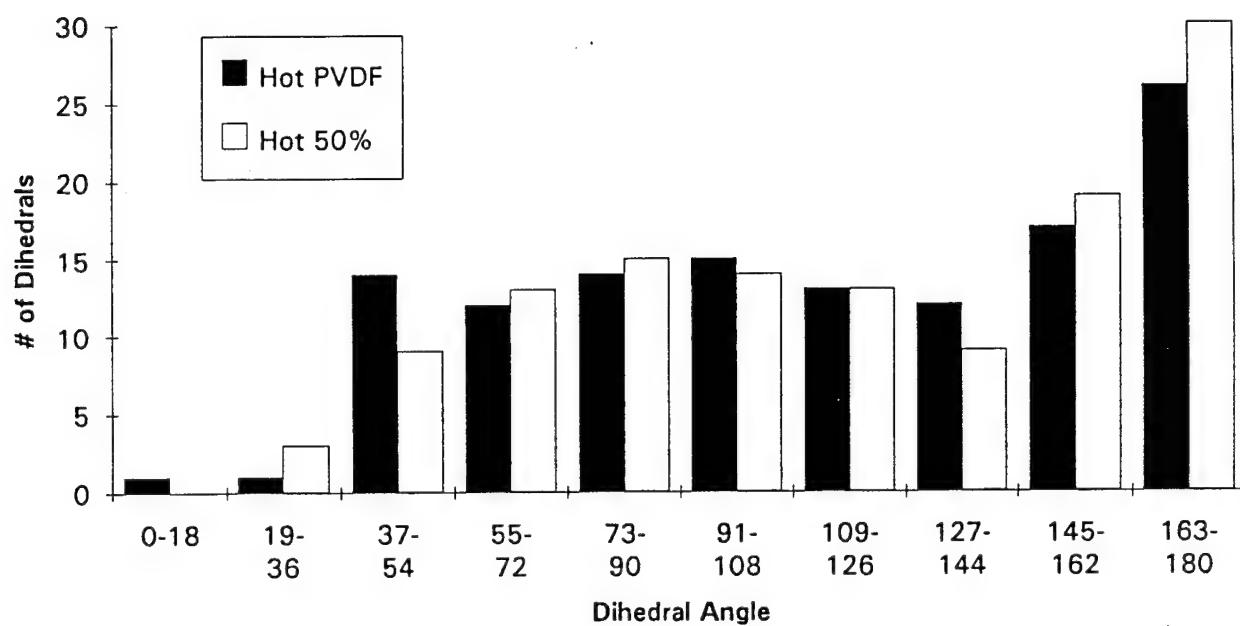


Figure 4. Histogram Showing Distribution of Dihedrals of Hot PVDF vs. Hot 50 mol% P(VDF-TrFE)

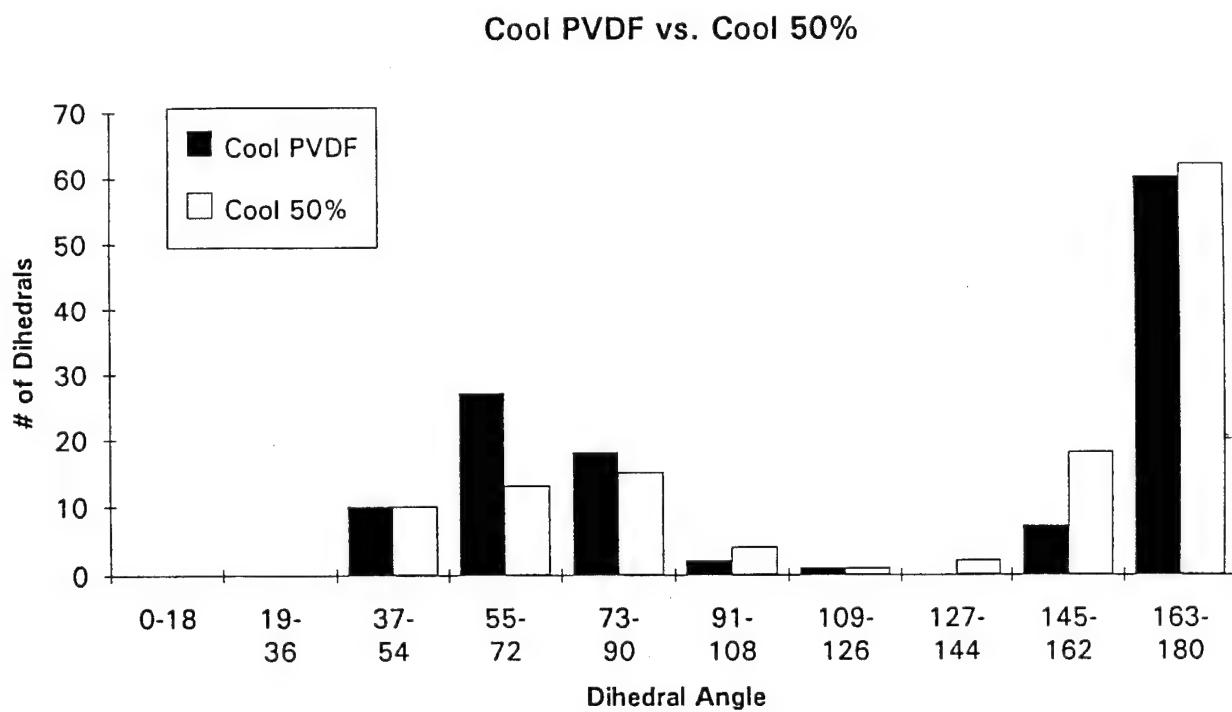


Figure 5. Histogram Showing Distribution of Dihedrals After Annealing

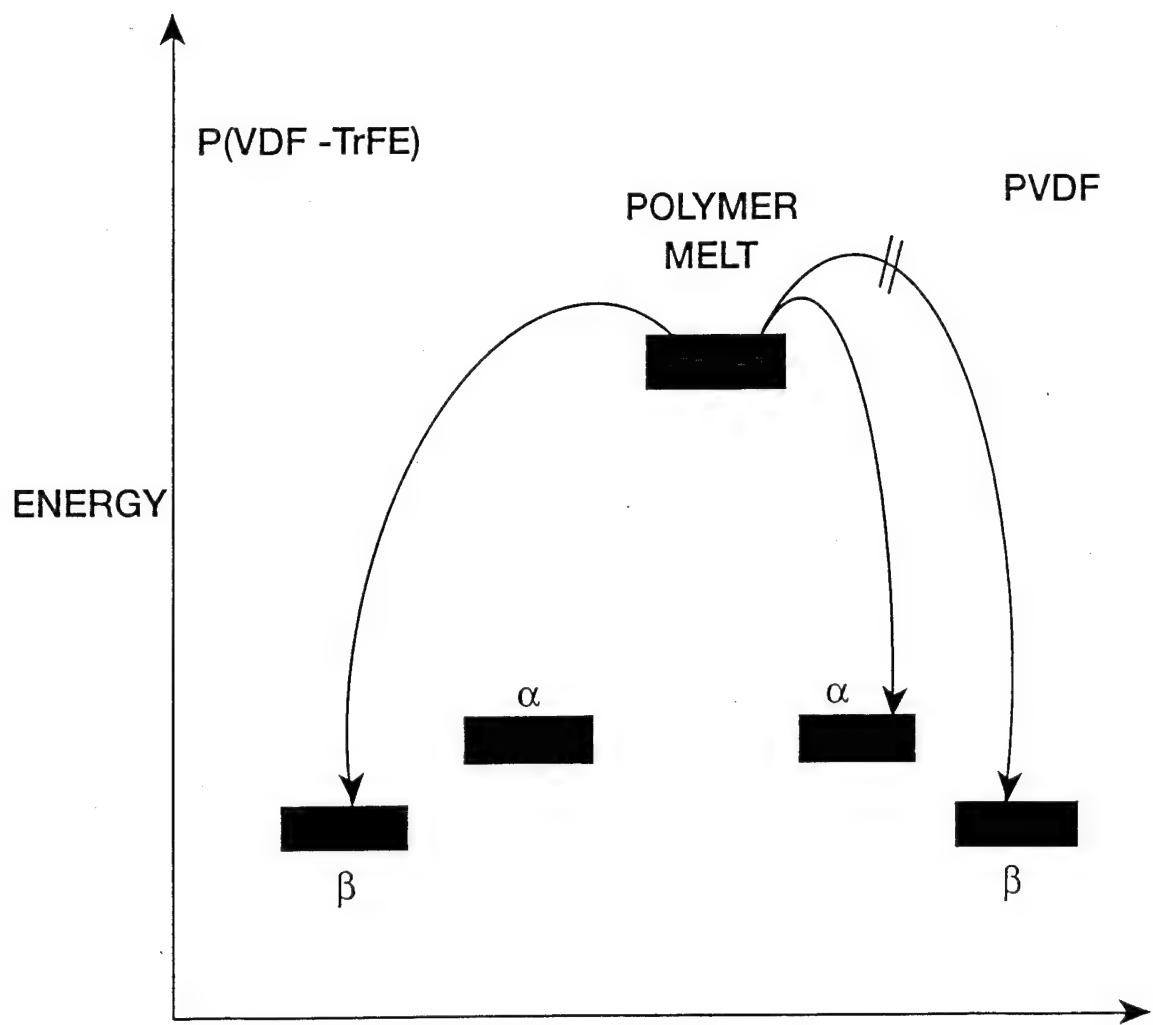


Figure 6. Energy Diagram

Table 1. Calculated Dihedral Angles of Simple Dimers

Dimer	Dihedral angle, deg
Vinylidene fluoride (hot)	-67.83
Vinylidene fluoride (cool)	-50.96
Vinylidene fluoride/trifluoroethylene (hot)	68.29
Vinylidene fluoride/trifluoroethylene (cool)	171.53

Table 2. Calculated gauche- and trans-Dihedral Angles of 1,28-Methylene Unit Single Chain Polymers

Polymer	g/t	%t	%g	%other
all- <i>trans</i> PVDF (hot)	0.73	44	32	24
all- <i>trans</i> PVDF (cold)	0.82	54	44	2
all- <i>trans</i> 50 mol% P(VDF-TrFE) (hot)	0.64	47	30	23
all- <i>trans</i> 50 mol% P(VDF-TrFE) (cold)	0.46	67	30	3
<i>tgtg'</i> PVDF (hot)	0.69	43	30	27
<i>tgtg'</i> PVDF (cold)	0.90	51	47	2

Table 3. Calculated gauche- and trans-Dihedral Angles of U-Shaped Polymers

Polymer	g/t	%t	%g	%other
all-trans PVDF (hot)	0.64	47	30	23
all-trans PVDF (cold)	0.65	58	38	4
all-trans 50 mol% P(VDF-TrFE) (hot)	0.53	51	27	22
all-trans 50 mol% P(VDF-TrFE) (cold)	0.53	63	34	3

Table 4. Elongation of a tgtg' PVDF Tetramer as Monitored by Geometry Optimization

End-to-end distance (Å)	C-C-C-C dihedral angle, deg				
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
9.252	45	180	-45	180	45
9.502	83	175	-84	-174	83
9.752	98	173	-91	-172	89
10.002	154	171	-97	-168	124
10.252	170	169	-168	-166	176

REFERENCES

1. G. J. Kavarnos, "Molecular Modeling: An Approach for the Study of Piezoelectric Polymers," NUWC-NPT Technical Report 10,771, Naval Undersea Warfare Center Division, Newport, Rhode Island, 12 December 1994.
2. G. J. Kavarnos and R. W. Holman, "A Molecular Mechanics and Crystal Packing Study of the Effects of Fluorine Content in Poly(vinylidene fluoride) and Vinylidene Fluoride-Trifluoroethylene Copolymers," *Polymer*, vol. 35, 1994, p. 5586.
3. G. J. Kavarnos and E. A. McLaughlin, "Development of a High-Frequency Multilayer Copolymer Acoustic Projector," NUWC-NPT Technical Report 10,607, Naval Undersea Warfare Center Division, Newport, Rhode Island, 31 March 1994.
4. P. J. Flory, *Statistical Mechanics of Chain Molecules*, Hanser, Munich, 1989.
5. R. J. Young and P. A. Lovell, *Introduction to Polymers*, 2nd ed., Chapman and Hall, London, 1991, p. 283.
6. A. J. Lovinger, "Ferroelectric Polymers," *Science*, vol. 220, 1983, p. 1115.
7. R. Hasegawa, Y. Takahashi, Y., Chatani, and H. Tadakoro, "'Crystal Structures of Three Crystalline Forms of Poly(vinylidene fluoride)," *Polymer Journal*, vol. 3, 1972, p. 600.
8. W. W. Doll and J. B. Lando, "Polymorphism of Poly(vinylidene Fluoride). III. The Crystal Structure of Phase II," *J. Macromol. Sci.-Phys.*, vol. B4, 1970, p. 309.
9. M. A. Bachmann and J. B. Lando, "A Reexamination of the Crystal Structure of Phase II of Poly(vinylidene fluoride)," *Macromolecules*, vol. 14, 1981, p. 40.
10. N. Karasawa and W. A. Goddard, III, "Force fields, Structures, and Properties of Poly(vinylidene fluoride) Crystals," *Molecules*, vol. 25, 1992, p. 7268.
11. B. L. Farmer, A. J. Hopfinger, and J. B. Lando, "Polymorphism of Poly(vinylidene fluoride): Potential Energy Calculations of the Effects of Head-to-Head Units on the Chain Conformation and Packing of Poly(vinylidene fluoride)," *Journal of Applied Physics*, vol. 43, 1972, p. 4293.
12. N. L. Allinger, "Calculation of Molecular Structure and Energy by Force-Field Methods," *Advances in Physical Organic Chemistry*, vol. 13, 1976, p. 1.
13. J. M. Haile, *Molecular Dynamics Simulation: Elementary Methods*, Wiley, New York, 1992.

14. U. Burkert and N. Allinger, *Molecular Mechanics*, American Chemical Society, Washington, D. C., 1982.

INITIAL DISTRIBUTION LIST

Addresssee	No. of Copies
Office of Naval Research	
W. A. Smith (Code 332)	1
K. J. Wynne (Code 1113)	1
Pennsylvania State University (Materials Research Laboratory)	
L. Eric Cross	1
Qiming Zhang	1
Western Kentucky University	
R. W. Holman	1
South Dakota State University	
Lewis F. Brown	1
Rutgers University	
Jerome Scheinbeim	1
Brian Newman	1
Defense Technical Information Center	2